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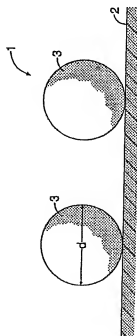
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(54) 【発明の名称】 水素貯蔵材

(57) 【要約】

【課題】 比較的軽量であって、常温、且つ低水素圧下にて高い水素貯蔵能力を有し、しかも水素吸放出速度の速い水素貯蔵材を提供する。

【解決手段】 水素貯蔵材1は、電気伝導性を持つ炭素材料よりなる複数の炭素担体2と、それら炭素担体2に担持された、水素吸着能を有する複数の微粒子3とを有する。微粒子3の担持量Aは $0.1 \text{ wt} \% \leq A \leq 2.0 \text{ wt} \%$ である。微粒子3は金属単体微粒子、合金微粒子および酸化物半導体微粒子から選択される少なくとも一種である。例えば、合金には、Mg、Ti、希土類元素、Zr、V、CaおよびAlから選択される少なくとも一種と、Fe、Co、Ni、Cu、Mn、MoおよびWから選択される少なくとも一種よりなる合金が該当する。



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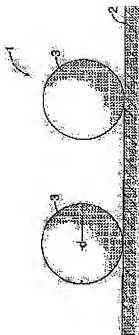
(21)Application number : 2001-342124 (71)Applicant : HONDA MOTOR CO LTD

(22)Date of filing : 07.11.2001 (72)Inventor : GOTO HAJIME
FURUTA TERUMI
TOKUNE TOSHIO
FUJIWARA YOSHINARI

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(54) HYDROGEN STORAGE MATERIAL



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage material which is rather lightweight and has high hydrogen storage ability at normal temperature and low hydrogen pressure and a fast absorption and emission rate of hydrogen.

SOLUTION: The hydrogen storage material 1 contains a plurality of carbon carriers 2 consisting of a carbon material having electric conductivity and a plurality of fine particles 3 having hydrogen adsorptivity carried by the carbon carrier 2. The proportion A of the fine particles 3 carried is in the range of 0.1 wt.% \leq A \leq 20 wt.%. The fine particles 3 are at

least one kind selected from single metal fine particles, alloy fine particles and oxide semiconductor fine particles. As for the alloy, for example, an alloy composed of at least one kind selected from Mg, Ti, rare earth elements, Zr, V, Ca and Al and at least one kind selected from Fe, Co, Ni, Cu, Mn, Mo and W is used.

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]Electrical conductivity. Have two or more carbon carriers (2) which consist of a carbon material which it has, and two or more particles (3) which have the hydrogen adsorption capacity supported by these carbon carriers (2), the holding amount A of the particle (3) is $0.1\text{wt}\% \leq A \leq 20\text{wt}\%$, and said particle (3) Metal simple substance particles, alloy particles. And as being chosen from an oxide semiconductor particle, are a kind as it is few, and said metal simple substance, As being chosen from V, Nb, Ta, Ti, Zr, Hf, La, and Ce, are a kind as it is few, and said alloy, That it is few as being chosen from Mg, Ti, a rare earth element, Zr and V, Ca, and aluminum A kind, Fe, Co, nickel, Cu, Mn, Mo. Become few from a kind to be chosen from W, and said oxide semiconductor And a Ni-oxide semiconductor, a Cr oxide semiconductor, a Cu oxide semiconductor, a Mn-oxide semiconductor, a Sn-oxide semiconductor, Zn oxide semiconductor, V oxide semiconductor, a Ti oxide semiconductor, Co oxide semiconductor. And hydrogen storage material characterized by a thing which is chosen from a Fe-oxide semiconductor, and which is a kind at least.

[Claim 2]The hydrogen storage material according to claim 1 whose mean particle diameter d of said particle (3) is $d \leq 1$ micrometer.

[Claim 3]The hydrogen storage material according to claim 1 or 2 as which said carbon carrier (2) is chosen from activated carbon, carbon black, a nanotube, and fullerene and which is a kind at least.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to hydrogen storage material, for example, suitable hydrogen storage material to use for the hydrogen storage machine of a fuel cell mounted vehicle.

[0002]

[Description of the Prior Art]So that the metal tunic which has the function to make a hydrogen content child dissociate to a hydrogen atom, on the surface of a porous carbon

material as this kind of hydrogen storage material may be formed and that hydrogen atom may be made to stick not only to the surface of a porous carbon material but to its inside conventionally. What was carried out is known (refer to JP,10-72201,A).

[0003]

[Problem(s) to be Solved by the Invention]However, since the porous carbon material surface is covered with the metal tunic in the conventional hydrogen storage material, Since it is required for the hydrogen adsorption sites on the surface of a carbon material to decrease in number, and for a hydrogen atom to diffuse the inside of a metal tunic at the time of the absorption/emission of hydrogen, according to it, the absorption/emission speed of hydrogen becomes slow, and, moreover, cool hydrogen storage material to about -196 ** which is liquid nitrogen temperature at the time of hydrogen absorption, and. Since the flood matter pressure of 5.1 or more MPa was needed preferably, there were 3 or more MPa of problems that facility cost increased.

[0004]

[Means for Solving the Problem]This invention is comparatively lightweight, and has high hydrogen storage ability by ordinary temperature and low-water-flow matter pressing down, and an object of this invention is to provide said hydrogen storage material with a quick hydrogen absorption/emission speed moreover.

[0005]Two or more carbon carriers which consist of a carbon material with electrical conductivity according to this invention in order to attain said purpose, Hydrogen adsorption capacity supported by these carbon carriers. Two or more particles which it has. Have, the holding amount A of the particle is $0.1\text{wt}\% \leq A \leq 20\text{wt}\%$, and as being chosen from metal simple substance particles, alloy particles, and an oxide semiconductor particle, said particle is a kind as it is few, and said metal simple substance V, Nb, Ta, Ti, Zr, Hf, La. And as being chosen from Ce, are a kind as it is few, and said alloy, That it is few as being chosen from Mg, Ti, a rare earth element, Zr and V, Ca, and aluminum A kind, Fe, Co, nickel, Cu, Mn, Mo. Become few from a kind to be chosen from W, and said oxide semiconductor And a Ni-oxide semiconductor, a Cr oxide semiconductor, a Cu oxide semiconductor, a Mn-oxide semiconductor, a Sn-oxide semiconductor, Zn oxide semiconductor, V oxide semiconductor, a Ti oxide semiconductor, Co oxide semiconductor. And hydrogen storage material which is chosen from a Fe-oxide semiconductor and which is a kind at least is provided.

[0006]As mentioned above, if hydrogen storage material is constituted from two or more carbon carriers and two or more particles supported by it, it is possible to attain a weight saving of the hydrogen storage material.

[0007]Particles of said composition attract an electron from one or more hydrogen

adhering to the surface in ordinary temperature and low-water-flow matter pressing down, An electron is attracted via a carbon carrier of electrical conductivity from one or more hydrogen near the particle which adsorbed one or more hydrogen of an ionic state, and adhered to the carbon carrier surface, and one or more hydrogen of an ionic state is made to stick to the carbon carrier surface. Suction of an electron through this carbon carrier is generated also about hydrogen adhering to both the particle surface and the carbon carrier surface. In this case, it is possible by setting up a holding amount of particles as mentioned above to secure widely a hydrogen adsorption site in the carbon carrier surface.

[0008]According to such a hydrogen adsorption mechanism, hydrogen storage material demonstrates high hydrogen storage ability by ordinary temperature and low-water-flow matter pressing down. Since the particle surface and the carbon carrier surface are adsorbed directly, the adsorption rate of hydrogen is quick, and since it moreover secedes easily from said surface with heating (or decompression), the releasing speed is quick.

[0009]However, a portion to which the holding amount A of particles cannot participate in adsorption of hydrogen to a field which consists among these both particles in a carbon carrier by distance between adjacency **** particles becoming large at $A < 0.1\text{wt}\%$ arises. This is because width of an accumulation layer of particles and an electron formed between carbon or a depletion layer is restricted. On the other hand, at $A > 20\text{wt}\%$, hydrogen adsorption sites on the surface of a carbon carrier decrease in number.

[0010]

[Embodiment of the Invention]The hydrogen storage material 1 consists of two or more carbon carriers 2 which consist of a carbon material with electrical conductivity, and two or more particles 3 which have the hydrogen adsorption capacity supported by these carbon carriers 2 in drawing 1. The holding amount A of the particle 3 is set up to $0.1\text{wt}\% \leq A \leq 20\text{wt}\%$.

[0011]As being chosen from metal simple substance particles, alloy particles, and an oxide semiconductor particle, the particles 3 are kinds as it is few. A kind corresponds that it is few to a metal simple substance as being chosen from V, Nb, Ta, Ti, Zr, Hf, La, and Ce. The thing which is chosen from Mg, Ti, a rare earth element, Zr and V, Ca, and aluminum, which is chosen from a kind, Fe and Co, nickel, Cu, Mn, Mo, and W at least and which consists of kinds at least corresponds to an alloy. Furthermore, a kind corresponds that it is few to an oxide semiconductor as being chosen from a Ni-oxide semiconductor, a Cr oxide semiconductor, a Cu oxide semiconductor, a Mn-oxide

semiconductor, a Sn-oxide semiconductor, Zn oxide semiconductor, V oxide semiconductor, a Ti oxide semiconductor, Co oxide semiconductor, and a Fe-oxide semiconductor.

[0012]As the carbon carrier 2, from a viewpoint of support of the particles 3, and hydrogen adsorption, a kind is used as what has large specific surface area being preferred, and being chosen from the activated carbon, the nanotube, and fullerene which are porous carbon materials as it is few. Use of carbon black is also possible.

[0013]As mentioned above, if the hydrogen storage material 1 is constituted from two or more carbon carriers 2 and two or more particles 3 supported by it, it is possible to attain the weight saving of the hydrogen storage material 1.

[0014]At the time of hydrogen storage, as shown in drawing 2, the low-water-flow matter pressure 4, for example, hydrogen of 1 or less MPa, is supplied to the ordinary temperature 1 into which it was put by the container, for example, 25 °C hydrogen storage material. Thereby, as shown in drawing 3, one or more hydrogen 4 adheres to the surface of the particles 3, and the surface of the carbon carrier 2.

[0015]As shown in drawing 4, the particles 3 attract electronic e^- from one or more hydrogen 4 adhering to the surface in ordinary temperature and low-water-flow matter pressing down. Electronic e^- is attracted via the carbon carrier 2 of electrical conductivity from one or more about three-particle hydrogen 4 which adsorbed the one or more hydrogen 4 of an ionic state, and adhered to the carbon carrier 2 surface, and the one or more hydrogen 4 of an ionic state is made to stick to the carbon carrier 2 surface. Suction of electronic e^- through this carbon carrier 2 is generated also about the hydrogen 4 adhering to both the particle 3 surface and the carbon carrier 2 surface. In this case, it is possible by setting up the holding amount of the particles 3 as mentioned above to secure widely the hydrogen adsorption site in the carbon carrier 2 surface.

[0016]The hydrogen storage material 1 demonstrates hydrogen storage ability high under ordinary temperature and hydrogen pressure according to such a hydrogen adsorption mechanism. Since the particle 3 surface and the carbon carrier 2 surface are adsorbed directly, the adsorption rate of the hydrogen 4 is quick, and since it moreover secedes easily from said surface with heating (or decompression), the releasing speed is quick.

[0017]The mean particle diameter d of the particles 3 is set as $d \leq 1$ micrometer. However, in $d > 1$ micrometer, in order to cause the increase of weight of hydrogen storage material, a weight merit is lost. The lower limit of the mean particle diameter d of the particles 3 is $d = 1$ nm preferably. In the particles 3, since the rate of a layer part of having an imperfect crystal increases to a high crystalline inside, the crystallinity of the

particles 3 falls and an exchange of an effective electron becomes impossible in $d < 1$ nm.
 [0018] Hereafter, an example is explained.

[0019] [An example - I]

A. As shown in manufacture (1) drawing 5 of a carbon nanotube, the high grade graphite pipe 5 the outer diameter of 6 mm, 3 mm in inside diameter, and 150 mm in length was prepared.

[0020] (2) By the weight ratio, the final ingredient ratio packed the catalyst 6 which mixes each powder of nickel, Y, Ti, and C (graphite) so that it may be set to nickel:Y:Ti:C=2:2:2:94 in the high grade graphite pipe 5, and manufactured the consumable electrode 7.

[0021] (3) As shown in drawing 6, evacuation of the inside of the chamber 9 of the arc discharge type carbon nanotube manufacturing installation 8 was carried out, subsequently, high grade helium replaced the inside of the chamber 9, and chamber pressure was adjusted to the manufacture pressure of 0.06MPa.

[0022] (4) voltage feedback control -- the voltage 35V and the current 100A -- power feed of the consumable electrode 7 which is the (+) pole is carried out, arc discharge is generated between the electrodes 10 which are the (-) poles, the consumable electrode 7 was exhausted by the arc discharge, and soot was generated so that it might become fixed.

[0023] (5) Synthetic soot was divided into three kinds, the thing adhering to a chamber wall, the thing deposited on the chamber bottom wall, and the thing of the shape of a nest of the spider, was collected, and recorded those weight. Among these, it became clear that the cobweb-like thing contained the carbon nanotube most. Thus, it became clear that the outer diameter D of the obtained carbon nanotube was in the range of $1.2 \text{ nm} \leq D \leq 1.6 \text{ nm}$.

[0024] B. Manufacture of hydrogen storage material [B-1]

** By the weight ratio, the 22.8 mg LaCl_3 powder and the 59.2-mg NiCl_2 powder by which weighing was carried out so that it might be set to La:nickel=1:5 were dissolved in 50-cc distilled water, and the solution was obtained. ** 34-mg Na_2CO_3 was added to the solution, it mixed, and settlings (carbonate) were obtained. ** The ** exception carried out settlings and it ranked second, and 80 **, the drying process of 1 hour, and 600 ** and calcining processing of 1.5 hours were performed one by one to the settlings, and the multiple oxide was obtained to them. ** 60-mg CaH_2 was added to a 38-mg multiple oxide, the mixture was prepared, it ranked second, 950 ** and heat-treatment of 1 hour were performed to the mixture in a hydrogen atmosphere, and output was acquired. ** Washing processing which used distilled water was performed twice to

output, it ranked second to it, and 80 ** and the drying process of 1 hour were performed. ** 74 mg of output and said 80-mg carbon tube were put in the chloride of 2N, it ranked second, and give an ultrasonic wave to the solution, and output was distributed, and the lime compound was removed out of the output. ** The ** exception carried out solid content, subsequently to the solid content washing processing which used distilled water was performed twice, and 80 ** and the drying process of 1 hour were performed after that.

[0025]The hydrogen storage material which made the carbon nanotube as a carbon carrier support the LaNi₅ particles as particles was obtained through each above process. It became clear that the holding amount A of the LaNi₅ particles in this hydrogen storage material was A=20wt% from a thermometric analysis result. When the particle diameter D of LaNi₅ particles is in the range of $10\text{ nm} \leq D \leq 1\text{ micrometer}$ from TEM and a SEM audit observation and the mean particle diameter \bar{d} was computed based on said result, it became clear that it was $\bar{d} = 0.5\text{ micrometer}$. This hydrogen storage material is made into Example 1.

[0026][B-2]

** 5-mg NiCl₂ powder and 4 mg of Mg powder were mixed in 10-cc dimethylformamide, and the solution was obtained. ** Said 100-mg carbon nanotube was mixed in the solution, and dispersion liquid were obtained. ** NiBr₂ and a methyl cyanide were added to dispersion liquid, it mixed, and settlings were obtained. ** The ** exception carried out settlings and, subsequently to the settlings, 560 ** and heat-treatment of 2 hours were performed one by one in argon atmosphere with 80 ** and the drying process of 1 hour.

[0027]The hydrogen storage material which made the carbon nanotube as a carbon carrier support Mg₂ Ni particle as particles was obtained through each above process. It became clear that the holding amount A of Mg₂ Ni particle in this hydrogen storage material was A=0.5wt% from a thermometric analysis result. When the particle diameter D of Mg₂ Ni particle is in the range of $1\text{ nm} \leq D \leq 1\text{ micrometer}$ from TEM and a SEM audit observation and the mean particle diameter \bar{d} was computed based on said result, it became clear that it was $\bar{d} = 0.3\text{ micrometer}$. This hydrogen storage material is made into Example 2.

[0028][B-3]

**1. The mixture of TiCl₄ of four g and 1.3-g NiCl₂ was hydrolyzed, and settlings (hydrous multiple oxide) were obtained. ** The ** exception carried out settlings and it ranked second, and 80 **, the drying process of 1 hour, and 600 ** and calcining processing of 1.5 hours were performed one by one to the settlings, and the anhydrous

multiple oxide was obtained to them. **1. 3-g CaH_2 was added to the anhydrous multiple oxide of five g, the mixture was prepared, it ranked second, 900 ** and heat-treatment of 0.5 hour were performed to the mixture in a hydrogen atmosphere, and powder was obtained. ** Washing processing which used distilled water for powder was performed twice, and, subsequently 80 ** and the drying process of 1 hour were performed.

[0029]Thus, when analyzed about the obtained powder using SEM-EDX, it became clear that this powder consisted of an aggregate of TiNi particles, TiO_2 particles, and NiO particles. When the particle diameter D of this aggregate is in the range of 50 $\text{nm} \leq D < 1 \mu\text{m}$, respectively and the mean particle diameter d was computed based on said result from TEM and a SEM audit observation, it became clear that it was $d = 0.6 \mu\text{m}$.

[0030]Then, mix the 10 mg of powder and 90 mg of activated carbon, and it ranks second so that the content of the powder which consists of an aggregate of TiNi particles, TiO_2 particles, and NiO particles may be 10wt%, Ball milling of low energy was given to the mixture in argon atmosphere, and the hydrogen storage material which made the activated carbon as a carbon carrier support the TiNi particles, TiO_2 particles, and NiO particles as particles was obtained. It became clear that the holding amount A of said powder in this hydrogen storage material was $A = 10\text{wt}\%$ from a thermometric analysis result. This hydrogen absorption material is made into Example 3.

[0031]C. The hydrogen storage ability example 1 of hydrogen storage material is put in in a container, subsequently Example 1 is heated to 500 ** using a heater, vacuum suction is performed in a container under the temperature, degasifying is performed, after that, Example 1 was cooled and the temperature was dropped to 25 ** which is ordinary temperature.

[0032]And when hydrogen was made to flow under application of pressure in a container and the hydrogen pressure in a container reached 0.1MPa, the inflow was stopped and the amount of hydrogen storage of Example 1 was measured. In this case, convergence time is set up in 10 minutes and this is below the same.

[0033]Next, when performed said same degasifying and the temperature reduction to ordinary temperature one by one, hydrogen was made to flow under application of pressure in a container after that and the hydrogen pressure in a container reached 0.2MPa, the inflow was stopped and the amount of hydrogen storage of Example 1 was measured.

[0034]Henceforth, said same operation was performed [having addressing/ to 0.1MPa /-raised the hydrogen pressure in a container], and when the hydrogen storage ability

of Example 1 was investigated until the hydrogen pressure in a container resulted in 0.9MPa, the result of drawing 7 was obtained.

[0035]When said same measurement was performed about Examples 2 and 3 on the same conditions as the above, drawing 8 and the result of 9 were obtained [except / of having set said cooking temperature as 300 ** about Example 2], respectively.

[0036]The amount of hydrogen storage of Example 1 is more than 5wt% in ordinary temperature and low-water-flow matter pressing down, i.e., 25 **, and 0.9MPa, and the amount of hydrogen storage of Example 2 is more than 4wt% in ordinary temperature and low-water-flow matter pressing down, i.e., 25 **, and 0.8MPa so that clearly from drawing 7 -9, Furthermore, it became clear that Example 3 had the high hydrogen storage ability that the amount of hydrogen storage is more than 5wt%, in ordinary temperature and low-water-flow matter pressing down, i.e., 25 **, and 0.4MPa.

[0037][Example-II] In argon atmosphere, the milling time was changed into the powder which consists of an aggregate of commercial TiNi particles, ball milling was given to it, and two or more powder which differs in the mean particle diameter d was obtained. The mean particle diameter d of TiNi particles was computed from TEM and a SEM audit observation to said the appearance.

[0038]Subsequently, mix 97 mg of carbon black with 3 mg of the powder, and it ranks second so that the content of each powder may be 3wt%, Ball milling of low energy was given to the mixture in argon atmosphere, and the hydrogen storage material which made carbon black as a carbon carrier support the TiNi particles as particles was obtained. It became clear that the holding amount A of the TiNi particles in these hydrogen storage material was A=3wt% from a thermometric analysis result.

[0039]One hydrogen storage material is put in in a container, subsequently the hydrogen absorption material is heated to 550 ** using a heater, vacuum suction is performed in a container under the temperature, degasifying is performed, after that, hydrogen absorption material was cooled and the temperature was dropped to 25 ** which is ordinary temperature.

[0040]And when hydrogen was made to flow under application of pressure in a container and the hydrogen pressure in a container reached 1MPa, the inflow was stopped and the amount of hydrogen storage of hydrogen absorption material was measured. In this case, convergence time is set up in 10 minutes and this is below the same. Next, the amount of hydrogen storage was measured about the remaining hydrogen absorption material in said similar way.

[0041]When drawing 10 shows a measurement result and sets the mean particle diameter d of TiNi particles as $d \leq 1$ micrometer from drawing 10, it turns out that the

amount of hydrogen storage increases rapidly. This originates in the increase and the increase in a number in the electronic suction effect by a particle with a mean particle diameter of $d \leq 1$ micrometer.

[0042]

[Effect of the Invention]According to this invention, by constituting as mentioned above, it is comparatively lightweight, and has high hydrogen storage ability by ordinary temperature and low-water-flow matter pressing down, and, moreover, hydrogen storage material with a quick hydrogen absorption/emission speed can be provided.

[Translation done.]